Bull. Chem. Soc. Jpn., **68**, 3397—3402(1995)

Spectroscopic and Kinetic Studies on Volume Expansion Processes of Photoresponsive Polyacrylamide Microgels in Water

Masazumi Ishikawa,# Hiroaki Misawa,## Noboru Kitamura,###
Masahiro Irie,† and Hiroshi Masuhara*

Microphotoconversion Project,§ ERATO, Research Development Corporation of Japan,
15 Morimoto-cho, Shimogamo, Sakyo-ku, Kyoto 606

†Institute of Advanced Material Study, Kyushu University, Kasuga-koen 6-1, Kasuga, Fukuoka 816

(Received June 7, 1995)

Photostimulated volume expansion of polyacrylamide microgels (initial radius=11—235 μm) bearing triphenylmethyl cyanide moieties (AAm-TPMCN) in water was studied on the basis of simultaneous measurements of the degree of ionic dissociation (α) of TPMCN to TPM$^+$ (triphenylmethyl cation) and the gel radius. The time profile of the radius change, $r(t)$, was analyzed by a convolution relation between $r(t)$ and the time course of α ($\alpha(t)$). The characteristic time constants of the volume change, related to the cooperative diffusion coefficient of the gel network, were determined for AAm-TPMCN gels with various radii. The faster photoresponse time of the volume change for the smaller AAm-TPMCN gel was explained in terms of the diffusion theory of gel networks in water.

Polyacrylamide (AAm) and poly(acrylic acid) (AA) gels are known to show a large volume change in solution when the gels are subjected to an external stimulus such as a pH, solvent, or temperature change.[1)] For AAm or AA gels, the driving force of volume expansion is hydrolysis of the amide groups or ionization of the carboxylic groups caused by an external stimulus, respectively. This brings about a change in an osmotic pressure between the gel and the surrounding solution phase and then subsequent swelling of the gel by solvent molecules. Several research groups reported relationships between a chemical potential change (i.e., osmotic pressure change) and diffusion of polymer gel network. Experimental results on the volume change of AAm and AA gels were compared with those predicted by these relations.[2—5)] Nevertheless, volume change processes of the gel have never been discussed on the basis of driving force, since determination of the degree of hydrolysis or ionization of the chromophore in the gel is very difficult.

Previously, one of the authors (M. I.) reported that AAm gels containing a triphenylmethane leuco dye (TPMX where X=CN or OH) in water exhibited large volume expansion upon UV photoirradiation.[6,7)] In this case, driving force of the volume change was assigned to ionic dissociation of the excited singlet state of TPMX to TPM$^+$ (triphenylmethyl cation) and X$^-$. We also studied photoinduced volume change processes of AAm-TPMCN gels in water; we showed that the time response of volume expansion could be shortened by reducing the gel size from millimeter to micrometer.[8)] Another important characteristics of the AAm-TPMCN gel are spectroscopic properties of the TPM$^+$ chromophore produced by photoirradiation. Namely, TPMCN does not show absorption above 400 nm, whereas TPM$^+$ exhibits strong visible absorption around 630 nm. Therefore, the degree of photoionization of the chromophore, related to driving force of the volume change, is expected to be determined quantitatively on the basis of UV-vis absorption spectroscopy. In addition to absorption characteristics, TPM$^+$ possesses a viscosity-dependent fluorescence lifetime in a picosecond time regime. Actually, microviscosity changes during photoinduced volume expansion have been measured by picosecond time-resolved fluorescence spectroscopy.[9)]

In this paper, we report a relationship between the degree of photoionization of TPMCN in the gel (α) and

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#Present address: Research Center, Nissan Motor Co., Ltd., 1 Natsujima-cho, Yokosuka 237.

##Present address: Department of Mechanical Engineering, Faculty of Engineering, The University of Tokushima, 2-1 Minamijosanjima, Tokushima 770.

###Present address: Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060.

§Five-year term project, Oct. 1988—Sept. 1993.

All correspondence should be sent to the permanent address of H. Masuhara at Department of Applied Physics, Osaka University, Suita 565.

the volume expansion rate of rod-shaped AAm-TPMCN microgels in water on the basis of simultaneous measurements of the volume change and spectroscopic characteristics of TPM^+.[10] Kinetics of volume expansion processes of the gel were also discussed in detail.

Experimental

Materials: Free radical polymerization of a freshly-distilled dimethyl sulfoxide solution (3 mL) containing acrylamide (10 mmol), a vinyl derivative of TPMCN (0.1 mmol), N,N′-methylenebis(acrylamide) (0.12 mmol), and 2,2′-azobis(isobutyronitrile) (10 mg) in microcapillary glass tubes at 60 °C for 2.5 h afforded rod-shaped AAm-TPMCN microgels. Elemental analysis and ^{1}H NMR for the vinyl derivative of TPMCN have been reported elsewhere.[8] After polymerization, the microcapillary glass tube was washed with acetone and one side of the glass tube was broken to expose a rod-shaped gel. The gel was then washed with pure water prior to measurements. The length/diameter ratios of the gels used in this study were ca. 10, so that the samples were considered as roughly cylindrical gels.

Apparatus: For simultaneous measurements of UV absorption and volume change of an AAm-TPMCN microgel under photoirradiation, we set up a microscope system as schematically illustrated in Fig. 1. A quartz cell containing an AAm-TPMCN gel and water was set on the stage of an inverted optical microscope (Nikon, Diaphot), and the gel was irradiated by a 500 W Hg–Xe lamp (Ushio, XM501MD) through a UVD33S glass filter (Toshiba, $255<\lambda<380$ nm). For absorption measurements, monitoring light from a 100 W Hg-lamp was reflected by a dichroic mirror (DM) and focused to the gel through an objective lens (OL) of the microscope. Light which had passed through the gel (I) was collected by a condenser lens (CL), reflected by a half mirror (HM), and then introduced to a monochromator–photomultiplier–computer system via an optical fiber to monitor absorbance of TPM^+ in the gel. The incident monitoring light intensity (I_0) was determined under the same conditions without a gel. Experimental errors in determining I or I_0 were ±5%, which were mainly due to fluctuation of the Hg–Xe lamp intensity with time. Since the molar absorption coefficient (ε) at the absorption maximum of TPM^+ ($\lambda_{max}=623$ nm, $\varepsilon_{623}=1.8\times10^4$ $M^{-1}\,cm^{-1}$ where $M=mol\,dm^{-3}$) was too large to follow an absorbance change, we monitored absorbance at (535 ± 2) nm throughout the study ($\varepsilon_{535}=1.04\times10^4$ $M^{-1}\,cm^{-1}$). The gel radius was monitored by a CCD camera-video set attached to the microscope. To study volume expansion processes in detail, accumulated video data were analyzed by a computer imaging system (Zeiss, IBAS).

Results and Discussion

Size Effects on Photoinduced Volume Change: Microgels prepared in this study (initial gel radius; $R_0=$ 11—235 μm) showed photoinduced volume expansion in water analogous to millimeter-sized, disk-shaped AAm-TPMCN gels.[6,7] As reported in our previous publication, the volume change was highly dependent on R_0 and, the photoresponse time was faster for the smaller gel; *micrometer-size effects*.[8] For the gel with $R_0=11$ μm, typically, the volume change almost finished within one min, while the larger gel ($R_0=180$ μm) showed volume expansion over 30 min. The equilibrium gel volume (V) after prolonged UV irradiation was also examined as a function of R_0 and was confirmed to be independent of R_0; $V/V_0=5.6$—6.0, where V_0 represented the gel volume before photoirradiation. Millimeter-sized AAm-TPMCN gels exhibit volume expansion as large as ca. 18 ($=V/V_0$),[6] so that V/V_0 of 5.6—6.0 for the present gels is smaller than this value. However, since an equilibrium volume of the gel is known to be strongly dependent on the molar ratio of TPMCN to AAm and the content of cross-linking agents, relatively small V/V_0 ratios for the microgels will be improved by optimization of these conditions. The main drawback of the millimeter-sized gels is that the time response of

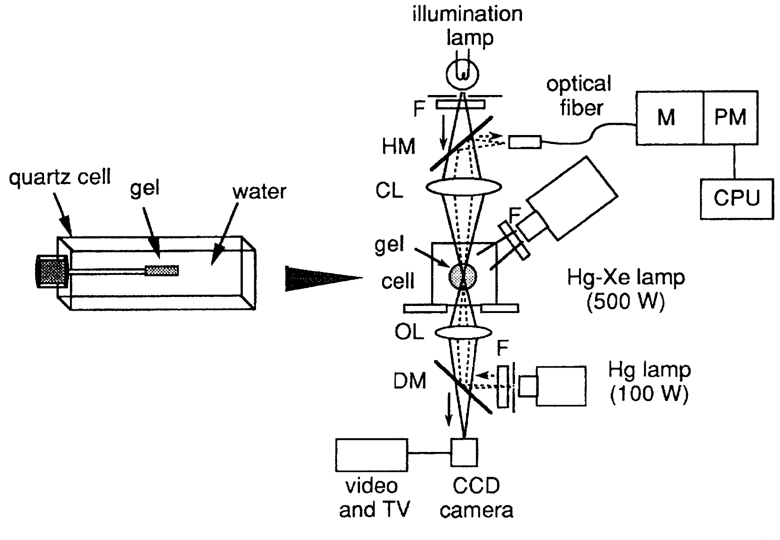

Fig. 1. An experimental setup for simultaneous measurements of absorbance and the radius of a AAm-TPMCN microgel in water. HM; half mirror, CL; condenser lens, OL; objective lens, DM; dichroic mirror, F; glass filter, M; monochromator, PM; photomultiplier tube.

the volume change is very slow (ca. 1 h).[6] Reduction of the gel size from millimeter to micrometer leads to large improvement of the photoresponse time, from the order of an hour to several seconds.

Simultaneous Measurements of UV Absorbance and Gel Volume: The time response profile of the gel volume cannot be fitted by a simple exponential function. This implies that the photoinduced volume change of the gel involves several elementary processes. Actually, the volume change is induced by photoionization of TPMCN and subsequent change in the osmotic pressure between the inner part of the gel and the surrounding water phase. This brings about volume expansion of the gel through uptake of a considerable amount of water (i.e., swelling). In order to obtain an inside look at volume expansion processes, the degree of ionization of TPMCN to TPM^+ (α) during photoirradiation should be determined precisely. Therefore, we conducted simultaneous measurements of time courses of α and the gel volume.

Typical examples of the photoresponse time profiles of the radius ($R(t)$) and absorbance of TPM^+ (Abs(t)) for the gel with R_0=98 μm are shown in Figs. 2a and 2b, respectively. The gel radius increased from 98 to ca. 140 μm in the initial stage of photoirradiation (irradiation time, t<60 s) and reached a constant value (ca. 160 μm) at t=150 s. On the other hand, absorbance of TPM^+ increased in a faster time scale as compared with $R(t)$; maximum absorbance (ca. 1.2) was observed at t=40 s. Further photoirradiation rendered a gradual decrease in absorbance to an equilibrium value (Abs ca. 0.9 at t=150 s). Clearly, $R(t)$ and Abs(t) do not coincide with each other.

The discrepancy between Abs(t) and $R(t)$ is readily understood, since the optical pathlength for determining absorbance of TPM^+ varies with the volume change; thus, observed absorbance does not correspond to the actual concentration of TPM^+ in the gel. In the present case, the optical pathlength is equal to the gel diameter at given t, so that the time course of the concentration of TPM^+ in the gel ($C^+(t)$) can be calculated by Eq. 1:

$$C^+(t) = \mathrm{Abs}(t)/2R(t)\varepsilon_{535} \quad (1)$$

On the other hand, the time profile of the degree of photoionization of TPMCN to TPM^+ in the gel ($\alpha(t)$) is given as in Eq. 2:

$$\alpha(t) = (C^+(t)/C_0)(R(t)^3/R_0^3) \quad (2)$$

where C_0 is the concentration of TPMCN in the gel at t=0 and can be estimated by the dry gel weight and the molar ratio of TPMCN to AAm (1:100). From Eqs. 1 and 2, we obtained the relation between $\alpha(t)$ and Abs(t) (Eq. 3):

$$\alpha(t) = \mathrm{Abs}(t)R(t)^2/2C_0R_0^3\varepsilon_{535} \quad (3)$$

$\alpha(t)$ thus calculated from observed Abs(t) and $R(t)$ is shown in Fig. 3. Under photoirradiation, α reaches an equilibrium value (ca. 0.8) at t≈60 s and does not decrease even after 60 s. Ionic dissociation of TPMCN almost finishes at t<60 s, while the gel radius gradually increases up to t≈150 s (Fig. 2a). The volume change is appreciably delayed compared with the time course of photoionization of TPMCN in the gel.

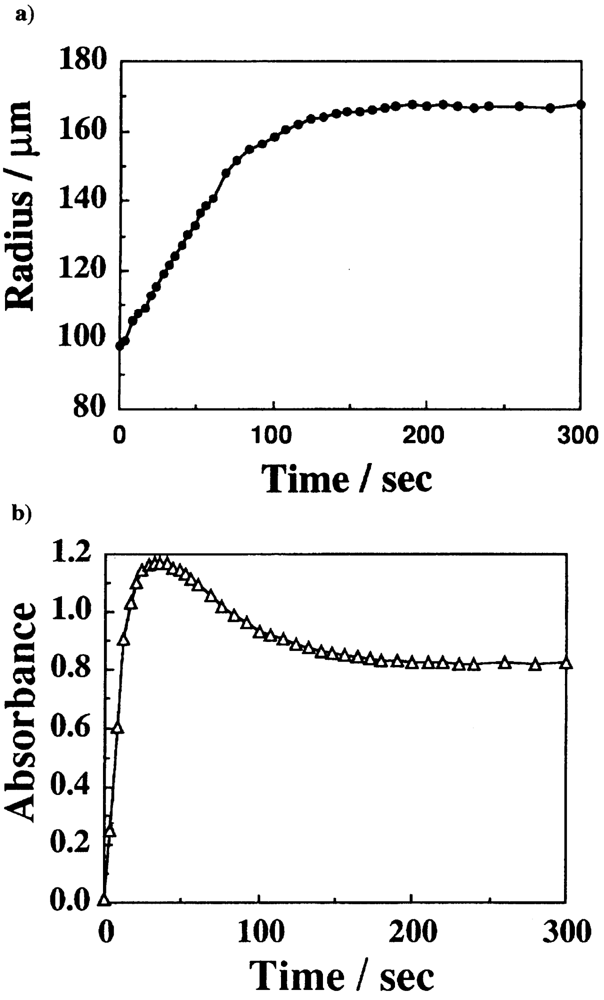

Fig. 2. Time response profiles of the gel radius (a) and absorbance of TPM^+ (b; at 535±2 nm) during photoirradiation. R_0=98 μm.

Kinetics of Photoinduced Volume Change: Tanaka and Fillmore[4] previously reported swelling behavior of spherical polyacrylamide gels and, demonstrated that time lag between the radius change and an external stimulus could be explained in terms of diffusion of the gel network. When an external stimulus is given instantaneously as an ideal case, relevant $R(t)$ can be described as in Eq. 4:

$$(R(t)-R_0)/(R_e-R_0) = 1-[\sum\{n^{-2}\exp(-n^2t/\tau)/\sum n^{-2}\}] \quad (4)$$
$$(n=1,2,3,\cdots)$$

where R_e is an equilibrium gel radius at $t=\infty$ and τ is a time constant determined by R_0.[11] Actually, they

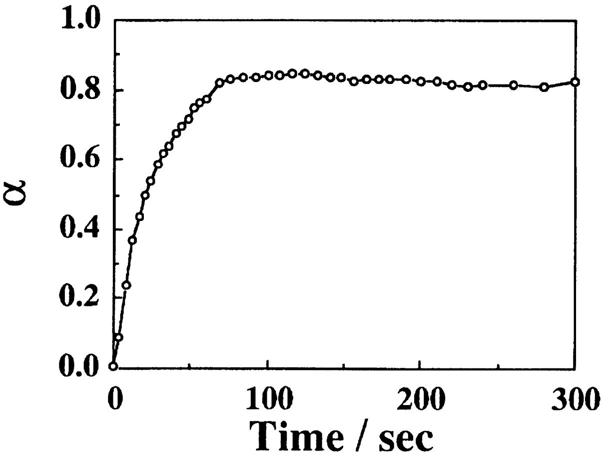

Fig. 3. Time response profile of the degree of photoionization of the TPMCN chromophore (α). R_0 = 98 µm.

reported that Eq. 4 could explain very well swelling behavior of polyacrylamide gels in water.[4] In the present experiments, on the other hand, $\alpha(t)$ increases gradually with time, as shown in Fig. 3, so that the gel radius is strongly affected by $\alpha(t)$. The delayed time response of the gel volume is related to both the noninstantaneous change of $\alpha(t)$ and diffusion of the gel network.

In order to confirm above discussions, the gel with R_0=101 µm was irradiated for 8 s and subsequent volume change in the dark was measured. The time profiles of the increment of the gel radius, defined as $r(t)$= $[(R(t)-R_0)/R_0]$, and relevant $\alpha(t)$ thus obtained are summarized in Fig. 4. Photoionization of TPMCN to TPM^+ proceeds only under UV irradiation, so that the α value shows a maximum at t=8 s and a very slow decrease with time owing to ionic recombination between TPM^+ and CN^-. On the other hand, $r(t)$ exhibits a slow rise profile up to t=100 s and levels off at t>100. The results indicate that delay of the radius change is governed mainly by diffusion of the gel network.

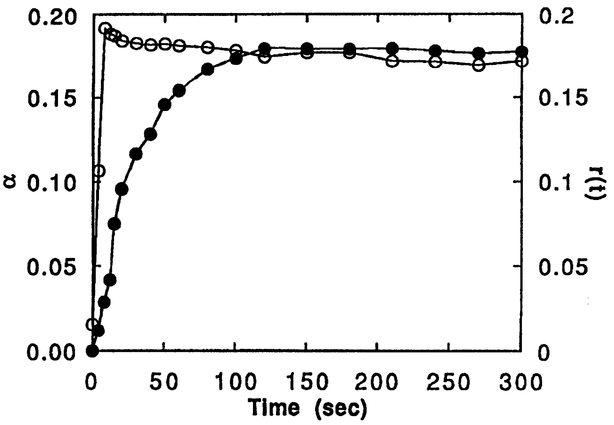

Fig. 4. Time response profiles of α (open circles) and $r(t)$ (closed circles) for the gel with R_0 = 101 µm. Photoirradiation was performed only for 8 s and, subsequent changes in the degree of ionization (α) and gel radius ($r(t)$) were determined in the dark.

Figure 4 demonstrates that both $\alpha(t)$ and $r(t)$ are almost constant at t>150 s. Therefore, a relationship between the gel radius and the α value in the equilibrium state can be derived. We determined the $\alpha(t)$ and $r(t)$ values at t=300 s in the dark after photoirradiation for 8 s (i.e., $r(t=300\text{ s})\sim r_e=(R_e-R_0)/R_0$)) analogous to the experiments in Fig. 4 and, these procedures were repeated to obtain a relationshinp between r_e and α. A plot of r_e against α falls on a very good straight line, as shown in Fig. 5 (correlation coefficient=0.995). For ordinary ionic gels, a change in three-dimensional polymer network caused by an osmotic pressure (Π) is described as in Eq. 6, Flory–Huggins' formula:[5,12]

$$\Pi=-\frac{NkT}{v}\left[\phi+\ln(1-\phi)+\frac{\Delta F}{2kT}\phi^2\right]$$
$$+\nu kT\left[\frac{\phi}{2\phi_0}-\left(\frac{\phi}{\phi_0}\right)^{\frac{1}{3}}\right]+\alpha\nu_1 kT\left(\frac{\phi}{\phi_0}\right)=0 \qquad (6)$$

In Eq. 6, the symbols are as follows: N=Avogadro's number; k=Boltzmann constant; T=temperature; v= molar volume of a solvent; ΔF=excess free energy for association between polymer segments and solvent; ϕ_0 and ϕ=volume fractions of the network at random walk and actual configurations in the gel, respectively; ν and ν_1=the number of constituent chains and the TPM^+ chromophore (ionic dissociative unit) per unit volume at $\phi=\phi_0$, respectively. Equation 6 can be simplified as in Eq. 7:[5]

$$(V'/V_0')^{2/3}\approx\alpha\nu_1 \qquad (7)$$

where V' is the volume of a gel and V_0' is that at a random walk configuration. For AAm-TPMCN gels, ν_1 is smaller than that of an ordinary ionic gel (AAm : TPMCN=100 : 1) and the observed volume change ratio $((R_e/R_0)^3-1)$ is ca. 5, so Eq. 7 holds in the present experiments. The linear relationship between r_e and α in Fig. 5 (slope=1.04) is therefore reasonably explained on the basis of the Flory–Huggins formula.

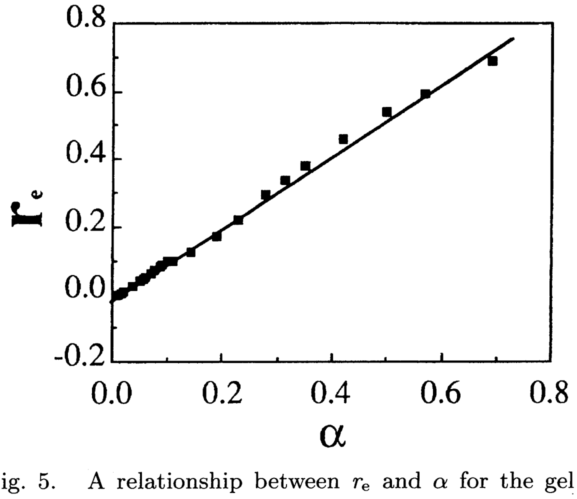

Fig. 5. A relationship between r_e and α for the gel with R_0=100 µm. See also the main text for explanation.

These results indicate that the equilibrium gel radius can be predicted by the α value, which is attained only by simultaneous measurements of the gel radius and absorbance of TPM^+ during the volume change.

Simulation of Photoinduced Volume Change: According to the results in Fig. 5, the slower radius change compared with the rate of TPM^+ generation will be simulated on the assumption that the equilibrium gel radius (i.e., r_e) is determined by $\alpha(t)$. In such a case, the radius change of the gel can be described by the following convolution equation (Eq. 8):[13]

$$r(t)=\int\{\mathrm{d}r_\mathrm{e}(t')/\mathrm{d}t'\}G(t-t')\mathrm{d}t' \tag{8}$$

where $r_\mathrm{e}(t)$ is the time profile of r_e and $G(t)$ has the form identical with the righth side of Eq. 4:

$$G(t)=1-\left[\sum\left\{n^{-2}\exp\left(-n^2t/\tau\right)/\sum n^{-2}\right\}\right] \tag{9}$$

The relationship between $r_\mathrm{e}(t)$ and $\alpha(t)$ is known from the plot in Fig. 5:

$$r_\mathrm{e}(t)=A\alpha(t)+B \tag{10}$$

with $A\approx 1.04$ and $B\approx 0$. Equation 8 can thus be rewritten as in Eq. 11:

$$r(t)=A\int\{\mathrm{d}\alpha(t')/\mathrm{d}t'\}G(t-t')\mathrm{d}t' \tag{11}$$

According to Eqs. 9 and 11, $r(t)$ is determined by $\alpha(t)$ and τ alone. Therefore, we can simulate the volume change processes of the gel with τ.

For the gel with R_0=101 μm the time response profile of the gel radius, $r(t)$, was simulated with the relevant $\alpha(t)$ data (Fig. 4) and τ, as shown in Fig. 6, in which observed (open circles) and simulated profiles (solid curve) were normalized to the gel radius at $t=300$ s. The observed data were best fitted by Eqs. 9 and 11 with τ=54 s. A very good agreement between the observed and simulated curves proves the validity of the present convolution analysis. The analysis was carried out for several gels with different R_0 and, the τ values obtained were plotted against R_0. As demonstrated in Fig. 7, the τ value is proportional to the square of R_0, and the time constant for the volume change (τ) was shown to decrease with decreasing the gel size. The micrometer size effects on the photoinduced volume change of the AAm-TPMCN gels in water can thus be reasonably explained in terms of the diffusion theory of the gel network.

The linear relationship in Fig. 7 affords a cooperative diffusion coefficient of the gel network (D) through the relation in Eq. 12:[4]

$$\tau={R_0}^2/(\pi^2D) \tag{12}$$

The intercept value of the plot in Fig. 7 gives $D=(1.1—1.5)\times10^{-7}\ \mathrm{cm^2\,s^{-1}}$, which is slightly smaller than the values reported for polyacrylamide gels: $(2.4—4.0)\times10^{-7}\ \mathrm{cm^2\,s^{-1}}$.[14,15] Li and Tanaka reported, however, that a cooperative diffusion coefficient of the network in a rod-shaped gel is 2/3 of that in relevant spherical gel,[15] so that the present D value for the AAm-TPMCN gel is not too small as compared with reported ones.

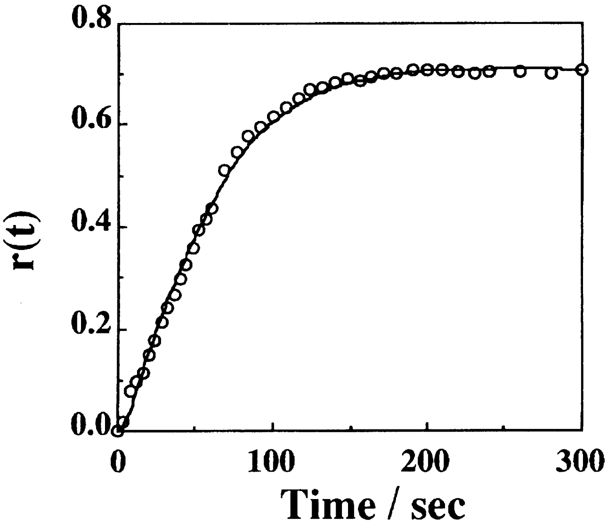

Fig. 6. Simulation (solid curve) of observed $r(t)$ (open circles) by the convolution method with τ=54 s. The time response profile of $\alpha(\alpha(t))$ for the gel with R_0= 101 μm shown in Fig. 4 was used for simulation.

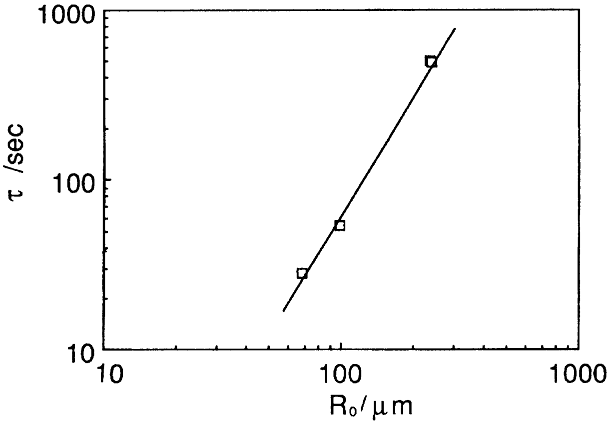

Fig. 7. A relationship between τ and R_0.

In order to know whether the τ value obtained by the present analysis is reasonable or not, we compared the results of photo- and solvent-induced volume changes for a AAm-TPMCN gel (R_0=235 μm).[16] The convolution analysis analogous to that for the data in Fig. 6 gave τ to be 500 s for both solvent- and photo-induced volume changes. Since τ is essentially governed by R_0 and D as in Eq. 12, the common τ value determined for both experiments indicates again the validity of the present analysis.

Conclusion

A microspectroscopic system was developed to study kinetics and mechanisms of photoinduced volume expansion of AAm-TPMCN microgels in water. Simultaneous measurements of the gel volume and visible absorption of TPM^+ revealed the characteristic behavior of the photoinduced volume change, showing time-delay of the volume change after photoionization of TPMCN. The origin of the micrometer size effects on the time constant of the volume change (i.e., photoresponse time) was also elucidated based on the convolution analysis of $r(t)$ and $\alpha(t)$. Such a study is possible only by direct measurements of driving force of the volume change ($\alpha(t)$) through observation of the degree of photoionization of TPMCN, as demonstrated in Figs. 3 and 4. Therefore, the TPMCN/TPM^+ chromophore is quite unique for obtaining an inside look at the mechanism and kinetics of swelling and shrinking processes of polymer gels; such a look cannot be attained in ordinary polymer gels without a dye chromophore. Furthermore, the present study clearly showed that microgels were superior to millimeter-order gels in the response time to a light signal. A light beam can thus be arbitrarily modulated and switched on/off. Photostimulated phenomena based on microgels will be promising to develop fast-response intelligent materials such as actuators or artificial muscles.

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16) The gel with $R_0=235$ μm, once measured for a photoinduced volume change in water, was soaked in an acetone–water mixture (7/13, vol/vol) for 3 h to shrink the gel and then, the solvent was changed to pure water under an optical microscope. Volume expansion of the gel followed by the solvent change was monitored analogous to that under photoirradiation.